

Edited by Robert M. Fitch

POLYMER COLLOIDS II

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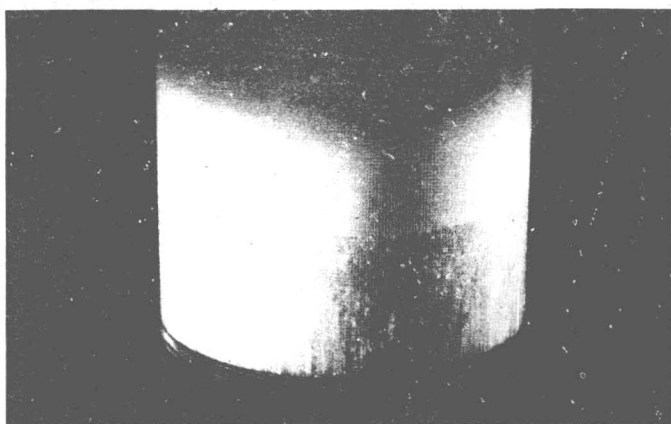
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Polycrystalline sediment displayed by a monodisperse polymethyl acrylate colloid. Magnification 2.5X (S. J. Liang and R. M. Fitch).



Iridescence of a stirred, monodisperse PVT colloid (see P. Bagchi, B. V. Gray, and S. M. Birnbaum, page 234). (Courtesy of Eastman Kodak Co.).

PREFACE

This volume is comprised of most of the papers presented at a symposium held in Miami Beach during the national meeting of the American Chemical Society in September, 1978. In a sense, it is a sequel to the first ACS symposium held on this topic and published under the title "Polymer Colloids" in 1971 by Plenum Press. That volume contained 12 papers, whereas "Polymer Colloids II" contains 33, an indication of the magnitude of the growth of the field in less than a decade.

Increased sophistication probably best characterizes the changes which have taken place, especially in the realm of instrumentation. Ten years ago techniques such as quasielastic light scattering, X-ray photoelectron spectroscopy (XPS - also known as ESCA), ion scattering spectroscopy (ISS), ultrasonic absorption spectroscopy and hydrodynamic exclusion chromatography (HEC) were unavailable to the polymer colloid chemist. Recent advances in all of these methods are described in this volume.

Although the book deals primarily with "synthetic latexes" or "emulsion polymers" as colloids, there are a number of papers which deal with their synthesis: particle nucleation in emulsion polymerization, the synthesis of emulsifier-free polymer colloids using novel reagents, molecular weight distributions derived from the kinetics of emulsion polymerization, and anionically polymerized non-aqueous polymer colloids. The kinetics and thermodynamics of the swelling of latex particles by monomers is also dealt with here. It has implications not only with regard to the kinetics of emulsion polymerization, but also to the formation of very large sized, monodisperse particles up to ca. 10 μm in diameter, along with the problem of the formation of "fines" in suspension or bead polymerization.

The largest section of this book deals with the surface chemistry of these systems. Polymer colloids have shown great promise as model colloids (See "Polymer Colloids" I) because they have spherical particles of various compositions, with extremely narrow size distributions. But they have proved perversely elusive as more

detailed information was sought concerning their surface chemistry. Recently some model polystyrene and polyvinyl toluene colloids have been synthesized which appear to overcome these obstacles. Adsorption of surface-active substances, both monomeric and polymeric, as a function of composition both of the adsorbate and adsorbent are described. These studies have implications in (1) colloid stability, (2) particle size determination in emulsion polymerization and (3) the theory of adsorption. To aid investigators, a new, rapid method of obtaining adsorption isotherms has been developed and reported.

Monodisperse latexes and inorganic sols may exhibit liquid-crystalline behavior as described in "Polymer Colloids" I. A great deal more has been learned about such systems during the past few years: they can be induced to form by the presence of very large concentrations of surfactant, the ordering of anisotropic particles may be highly shear-dependent, and the DLVO theory may be applied to the ordering process.

A variety of studies on the coagulation or flocculation of polymer colloids is described including (1) non-aqueous latexes that coagulate both as the temperature is raised and lowered past critical values, (2) monomer-induced aggregation, (3) coagulation of amphoteric colloids, and (4) flocculation by polyelectrolytes.

This book has been the result of the cooperative efforts of over 100 scientists. All the manuscripts were submitted to two reviewers, many of whom are outstanding leaders in the field, whose generous devotion of their time is gratefully acknowledged. Unfortunately they must remain nameless. Proofreading and indexing were performed by Shu-jan Liang, Tor Henrik Palmgren, Prakash Mallya, Christopher Fitch, Peter Tarcha and A.R.M. Azad. Especial thanks go to Charles Fifield who served as Assistant Editor.

My wife, Reta, has always given her support in many ways for which I am continually grateful.

Robert M. Fitch

Storrs, Connecticut

September 1979

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THE EXPANSION CHARACTERISTICS OF CARBOXYLIC EMULSION POLYMERS

I. PARTICLE EXPANSION DETERMINED BY SEDIMENTATION

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SUMMARY

Carboxylic monomers are often used as minor constituents in emulsion polymerization to impart desirable properties to latexes and latex films. Incorporated carboxyl groups can also have a major effect on latex viscosity as a result of particle expansion upon neutralization. Evidence from conductometric titrations suggests that carboxyl groups are often concentrated near the particle surface. The resultant model of an expanded particle is that of a hydrated acid-rich shell surrounding a compact polymer core. This model is used to develop an equation which can be used to estimate the thickness of the expanded layer as a function of pH, and a sedimentation method is described which permits a detailed study of the factors involved in particle expansion. Of particular concern are the effects of polymer concentration and ionic strength on the rate of particle sedimentation.

INTRODUCTION

Carboxylic monomers, such as acrylic acid, are included in latex polymerization recipes for a variety of reasons. One of the most important is the assumption that inclusion of acid groups will provide a means for increasing the surface charge of the latex particles. Since electrostatic repulsion is a basic tenet of modern theories of colloid stability, an increase in surface charge should improve the stability of latex suspensions. Indeed, both the freeze-thaw and mechanical stability of latexes can be effectively increased in this manner. The adhesion of latex films to many types of substrates is also promoted by the inclusion of carboxyl groups in the polymer. In addition, carboxylic monomers are frequently used

to introduce crosslinking sites into thermosetting films. Finally, the acid content of emulsion polymers has a profound effect on their rheological behavior. For these reasons, the nature of acid groups in carboxylic latexes is important from a fundamental as well as practical standpoint.

Of particular interest in latex design are the expansion characteristics of carboxylic particles upon neutralization. An example of the dramatic viscosity changes which can occur in carboxylic latexes as shown in Figure 1, in which the Brookfield viscosity of

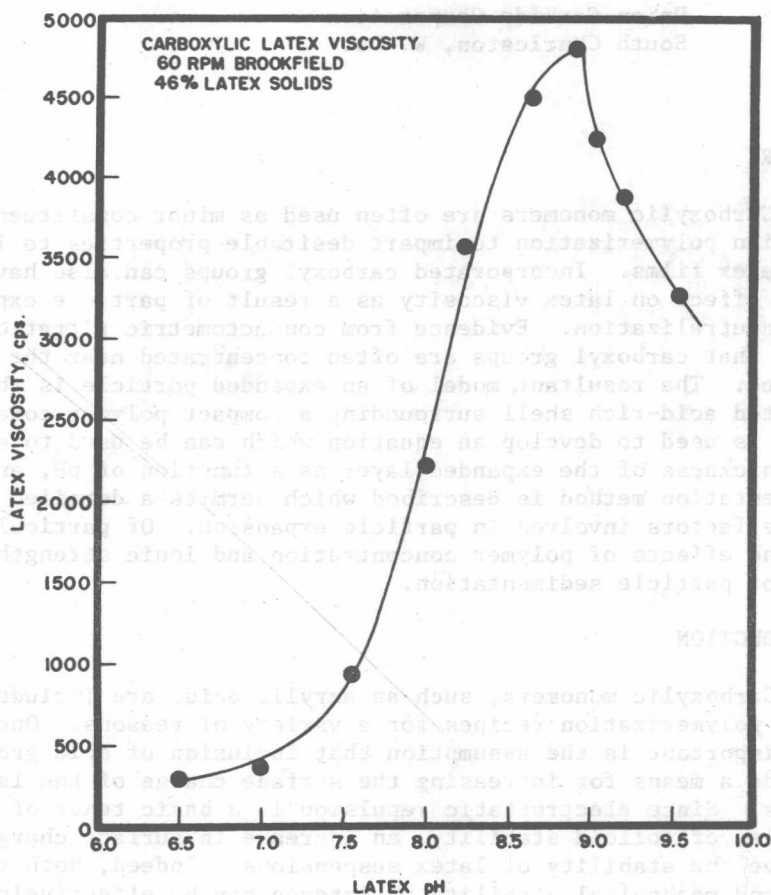


Fig. 1. Characteristic viscosity variation with neutralization of a carboxylic latex at high solids.

a latex containing acrylic acid is plotted as a function of pH. Viscosity control is especially difficult in such a system because of the narrow pH range over which the viscosity increase occurs. A thorough understanding of the phenomenon is required before it can be utilized or controlled. Previous studies of the alkaline swelling of latexes¹⁻³ have described the effects of various acids and polymer compositions, generally at high acid levels where considerable dissolution of the particles occurs. The present work is concerned with the distribution of acid groups in latex dispersions containing relatively low acid (2-3 percent), and the relative change in particle size with pH. In this report, a sedimentation method is described for quantitatively determining particle expansion so that a detailed study of the factors involved is possible.

EXPERIMENTAL

Latex Preparation

Model latexes were prepared by a semi-batch technique in which a monomer mix was fed into a reactor at 80°C in the presence of ammonium persulfate and a single anionic surfactant, Aerosol OT. The initial surfactant content of the reactor was adjusted to produce a particle size in the range of 0.10 to 0.50 μm . The monomer mix consisted of 40 parts methyl methacrylate, 54 parts ethyl acrylate and 6 parts butyl acrylate. The polymerization was arbitrarily divided into two stages, Stage I being the first half of the monomer feed, Stage II being the last half of the feed. Acrylic acid, amounting to 2 percent of the total monomer feed was added in either of the two stages or equally divided between the stages to prepare latexes with the same overall composition but with three different modes of acrylic acid addition. This describes the standard acrylic latex composition used throughout this study.

In addition, several polystyrene and poly(methylmethacrylate) latexes were prepared in the same manner for comparison. Since no buffer was used in the recipe, the pH of the latexes as made was approximately 2.5.

Conductometric Titrations

Titrations were carried out at 25°C in a thermostated cell designed by Mysels.⁴ Its essential feature is an annular volume through which the solution is continuously circulated from a main reservoir into which the titrant is added. Since the electrodes are in the annular space the cell constant does not vary as the solution is diluted. The cell constant was 8.4 cm^{-1} . This relatively high value enabled the cell to be used with mixtures of fairly high ionic strength, a desirable feature when working with latex dispersions. Conductance measurements were made with a Leeds and Northrup No. 4959 Electrolytic Conductivity Bridge

operating at 1000 cps. The galvanometer null detector provides a sensitivity of 1.0 percent of the conductance reading.

Acid distributions were determined by titrating a known quantity of latex with 0.1 N sodium hydroxide solution. A similar titration was carried out on the aqueous supernatant phase from which the particles had been removed by centrifugation. In each case strong and weak acid end points were observed. It was found that the end points of the supernatant titration could be sharpened considerably by diluting the sample with a 50% isopropanol/water mixture. The distribution of detectable weak acid between the water and polymer phases was calculated and compared with the amount of acrylic acid in the monomer charge. Any deficit was assumed to be buried in the particles and unavailable for neutralization.

Sedimentation Methods

A master batch of each latex was prepared by dilution with distilled water to the desired concentration, generally 1.0 percent by weight. Individual samples were taken and adjusted with concentrated sodium hydroxide solution to various pH values from 3 to 12 and allowed to equilibrate for 24 hours. Sedimentation rates were determined at 30°C with a Beckman Model E analytical ultracentrifuge. The operating speed was selected to give a sedimentation time of at least 20 minutes. With transmission optics, the sedimenting boundary was found to be very sharp for latexes having fairly narrow particles size distributions, and precise measurements of sedimentation coefficients could be obtained.

Acid Distributions

An obvious concern in dealing with carboxylic emulsion polymers is the location or distribution of the carboxyl groups. Three possibilities exist: the water phase, the particle surface and the particle interior. Conductometric titrations are conveniently used to determine the number of strong and weak acid groups in latexes since changes in ion mobilities indicate end points rather than changes in pH. Although the interpretation of conductometric titration plots is not always straightforward, the use of model systems generally simplifies the task. As described in the last section, three model latexes were prepared in which the acrylic acid was added in various ways to see if the acid distribution was strongly influenced by the mode of addition. The acid distributions for the three model acrylic latexes are given in Table I.

Although there are slight variations, the general conclusions reached from these results are that most of the carboxyl introduced into the system are titratable and that most of them are located in the surface region of the particles whether the acid was introduced

Table I. Distribution of Acrylic Acid in Standard Acrylic Latex By Conductometric Titration

Mode of Acid	Fraction of Total Acid Charged			
Addition	Surface	Soluble	Total	Buried
Stage I	0.98	0.01	0.99	0.01
Stage II	0.91	0.08	0.99	0.01
Stages I & II	0.99	0.02	1.01	0

early or late in the polymerization. The critical assumption made in this interpretation is that carboxyls within the particle interior can not be neutralized, at least not in the time frame of the titration.

If, in fact, the incorporated carboxyls are preferentially located near the particle surface, and if the viscosity increase illustrated in Figure 1 is due to particle swelling as a consequence of carboxylate salt formation, then the resultant model of an expanded particle is that of a hydrated acid-rich shell surrounding a compact polymer core. With this conclusion, the problem is reduced to determining, in situ, the thickness of the hydrated layer.

Particle Sedimentation

Sedimentation phenomena are of wide general interest and are of particular interest in latex studies. The rate of sedimentation of a particle is a function of its size, and many particle size measurement techniques are based on this fact. Since aggregation leads to a change in effective size, colloid stability can also be studied. Of special interest is the influence of adsorption and solvation on the hydrodynamic properties of latexes and dispersions in general, and sedimentation techniques are well suited for studying problems of this type. Although the following discussion deals primarily with latexes as an example of a colloidal system of spherical particles suspended in a liquid, the treatment is applicable to other types of dispersions provided the effect of particle shape is taken into consideration.

The central problem is a description of the sedimentation behavior of a sphere surrounded by a layer of another material. The model is one of a rigid core, possessing definite properties, and surrounding shell which does not penetrate the inner core. The "particle" (core and shell) is suspended in a liquid of known density. In a practical case, the core may be a latex particle and